PARTICULATE NITRATE MEASUREMENTS DURING CRPAQS

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OBJECTIVES

- Present nitrate measurements for different samplers, locations, and time periods
- Evaluate the extent of nitrate volatilization

INTEGRATED SAMPLERS

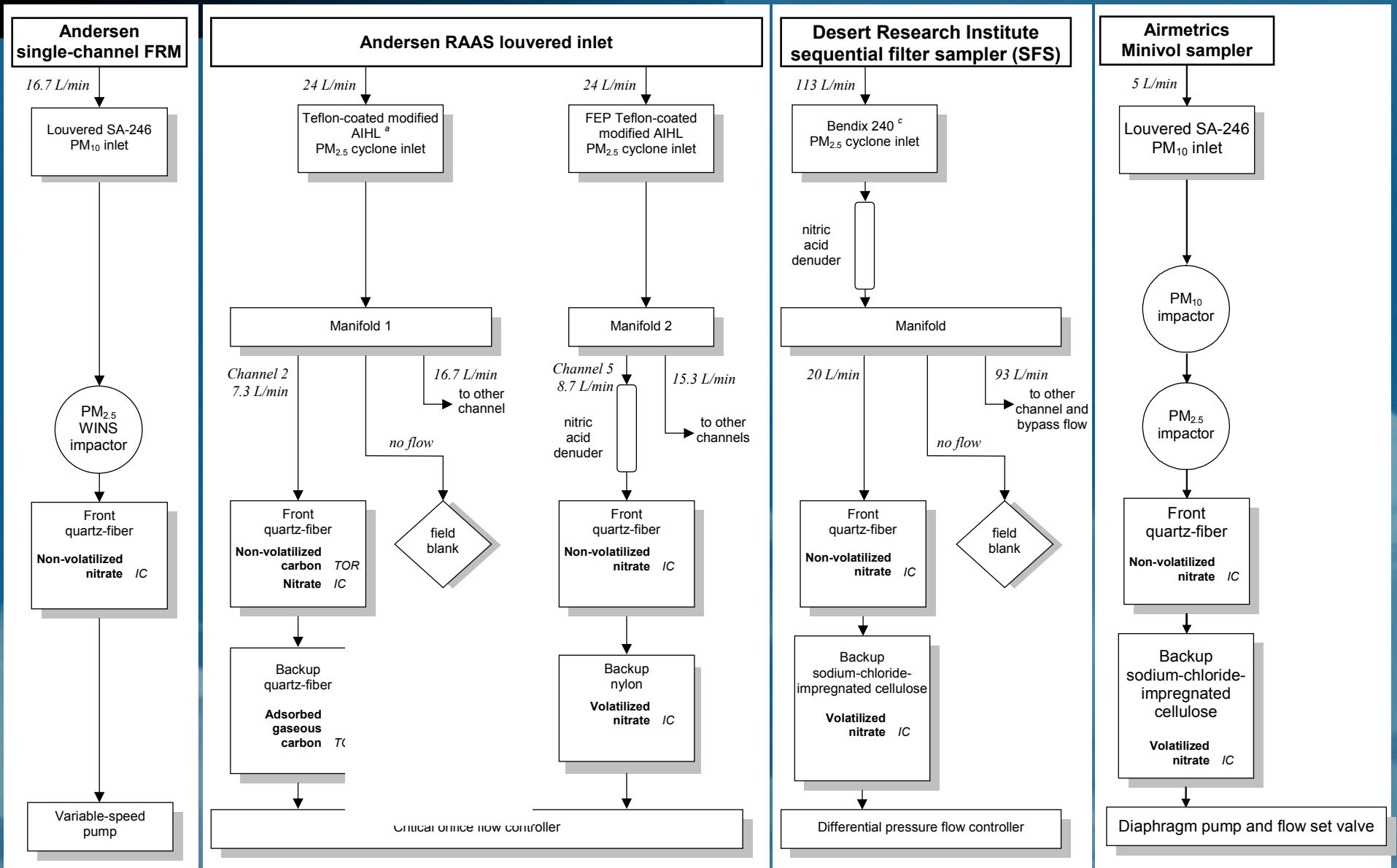
RAAS-100
single-channel $PM_{2.5}$ FRM sampler
Andersen Instruments, Smyrna, GA

RAAS-400
$PM_{2.5}$ speciation sampler
Andersen Instruments, Smyrna, GA

Dual-channel
sequential filter
sampler
Desert Research Institute, Reno, NV

Minivol sampler
Airmetrics, Eugene, OR

INTEGRATED SAMPLERS *(continued)*



TYPES OF INLETS

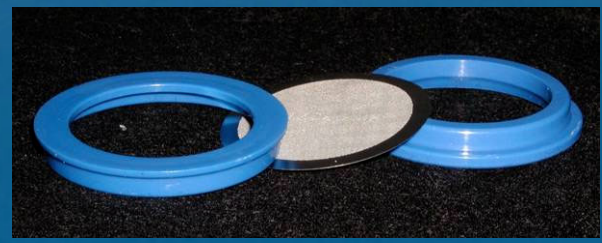
Type	Cut Point (d_{50})	Slope ($\sqrt{d_{84}/d_{16}}$)	Flow Rate
EPA WINS impactor (FRM)	2.48 µm	1.18	16.7 L/min
AIHL cyclone (RAAS)	2.5 µm	1.18	24 L/min
Bendix/Sensidyne 240 cyclone (SFS)	2.5 µm	1.7	113 L/min
Impactor (Minivol)	2.5 µm	1.23	5 L/min

TYPES OF DENUDERS

Sampling System	Denuder Type
FRM	None
RAAS	Sodium-carbonate-coated glass denuder (flow rate = 8.7 L/min)
SFS	Aluminum-oxide-coated tubular denuder (flow rate = 20 L/min)
Minivol	None

TYPES OF FILTER HOLDERS

	Inlet surface	Filter holder
FRM	Anodized aluminum	Delrin ring with stainless steel grid
RAAS	FEP Teflon coated	Delrin ring, polycarbonate holder
SFS	Anodized aluminum	Nuclepore polycarbonate holder
Minivol	Anodized aluminum	Nuclepore polycarbonate holder



SAMPLING SUBSTRATES FOR ION CHROMATOGRAPHY ANALYSIS

Analyte	Filter type	Sampling system
Non-volatilized NO_3^-	Pallflex #2500 QAT-UP quartz-fiber	FRM RAAS SFS Minivol
Volatilized NO_3^-	Schleicher & Schuell #66 nylon	RAAS
Volatilized NO_3^-	Whatman 31ET cellulose-fiber impregnated with NaCl	SFS Minivol

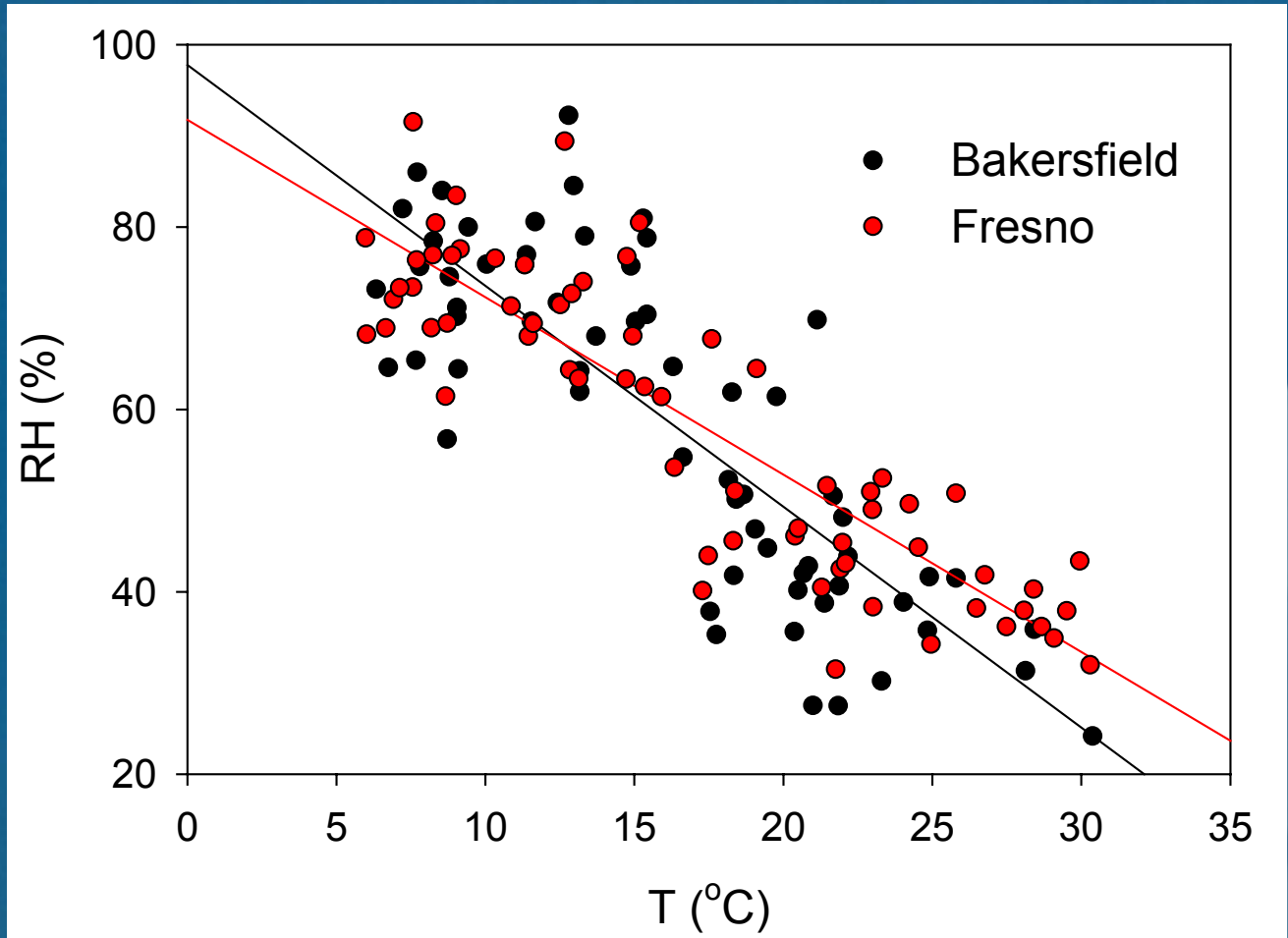
THE AMMONIUM NITRATE EQUILIBRIUM

$NH_4NO_{3\ (p)}$ <=> $NH_{3\ (g)} + HNO_{3\ (g)}$

low T, high RH <=> high T, low RH

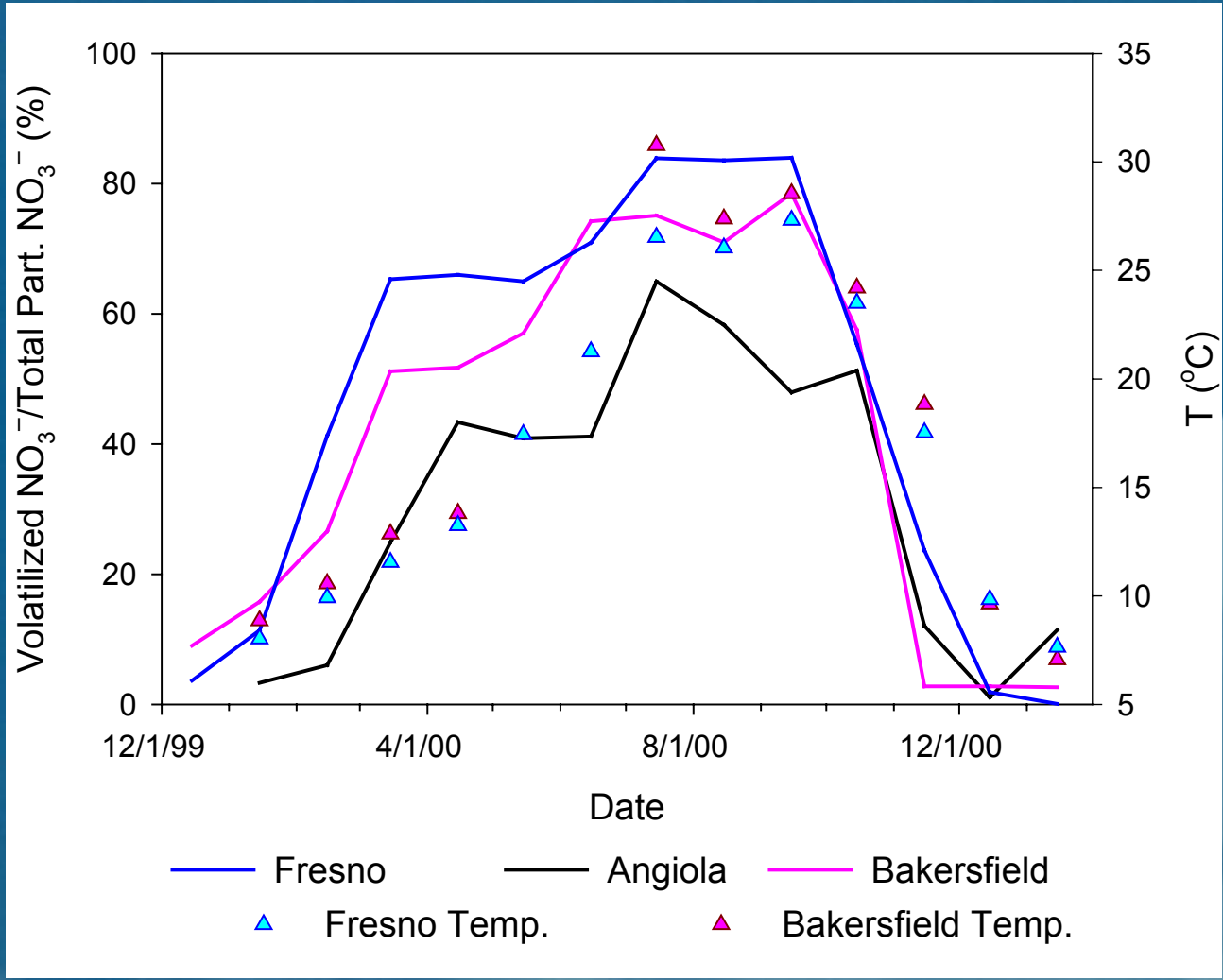
24-HOUR AVERAGE TEMPERATURE (T) AND RELATIVE HUMIDITY (RH) (Dec. 1999–Jan. 2001)

T and RH are similar at both sites and vary inversely.



MONTHLY AVERAGE NITRATE VOLATILIZATION

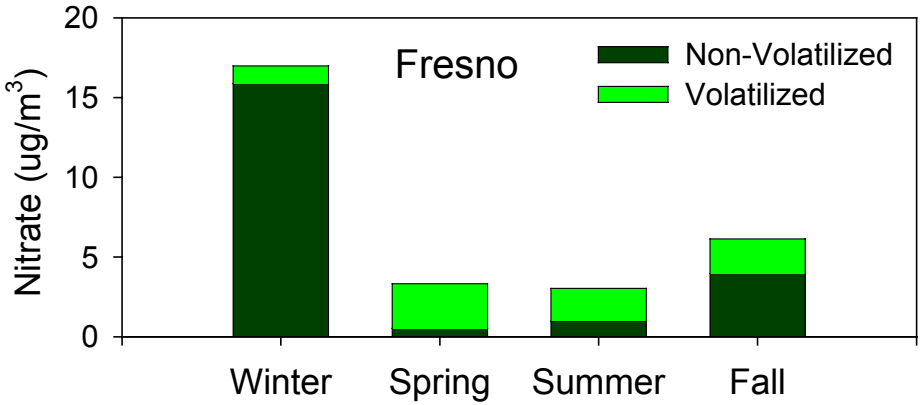
Peaks during warmer months. Relatively less volatilization at Angiola.

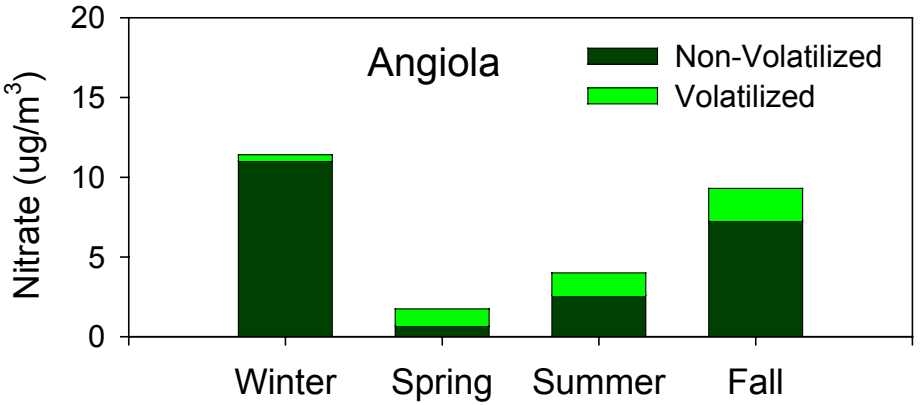


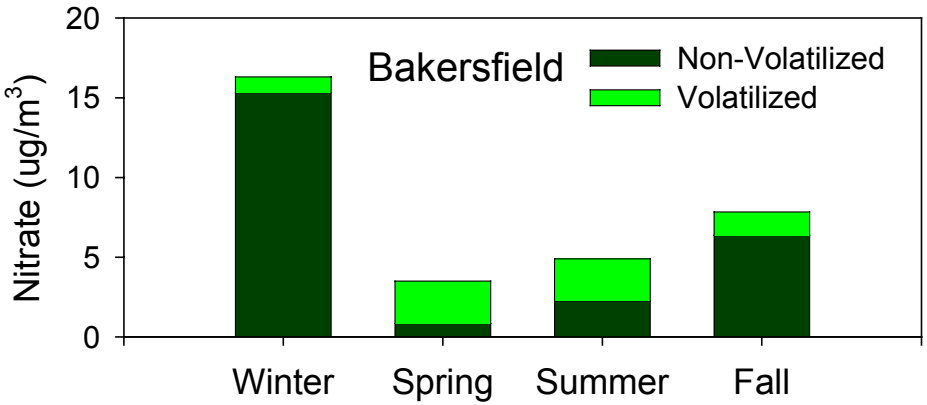
$PM_{2.5}$ PARTICULATE NITRATE (PNO_3^-)

Peaks in winter and fall.

Volatilization is highest in spring and summer at the two urban sites.

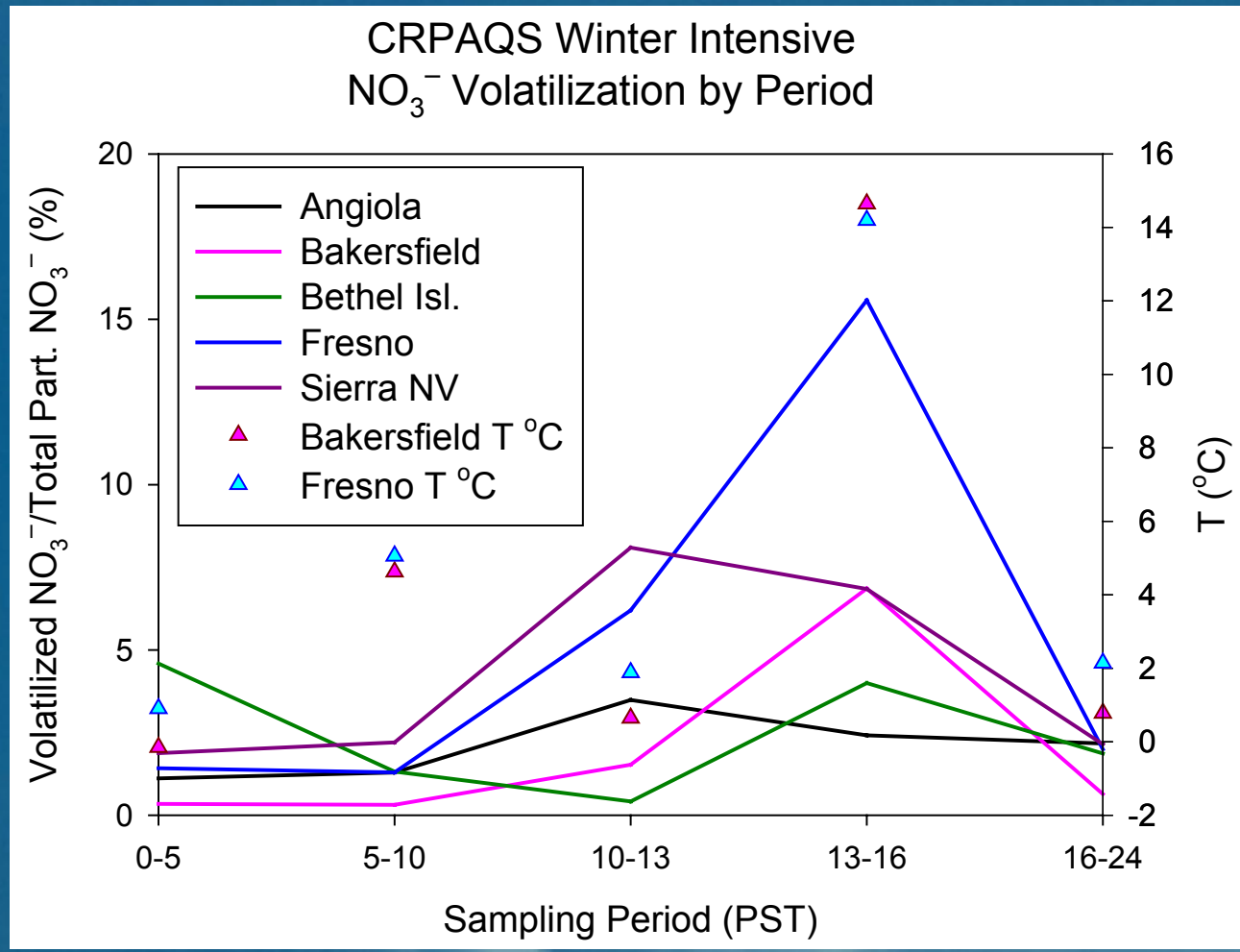






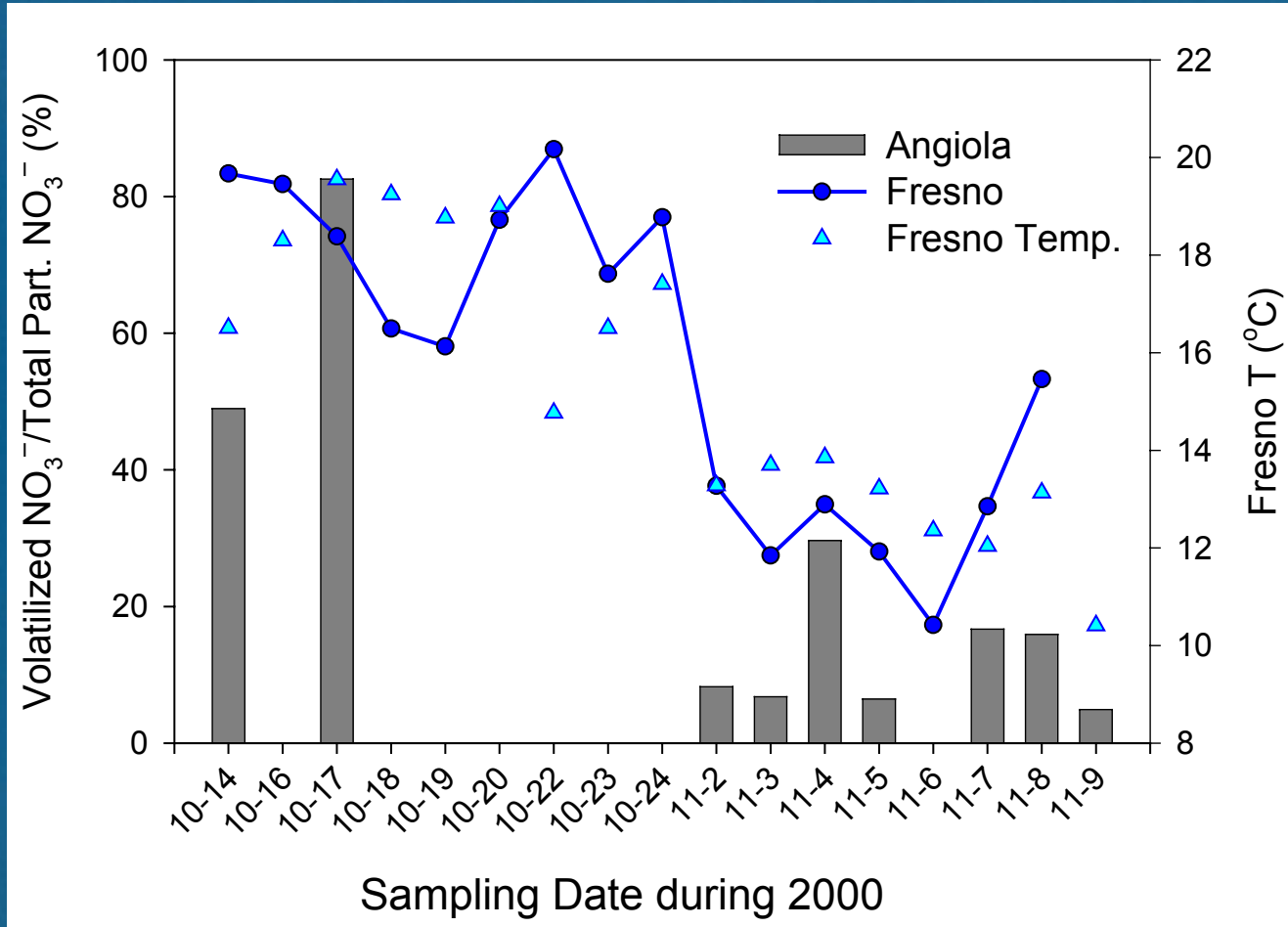
WINTER INTENSIVE NITRATE VOLATILIZATION BY SAMPLE PERIOD

Nitrate volatilization increases throughout the day with temperature, even in winter.



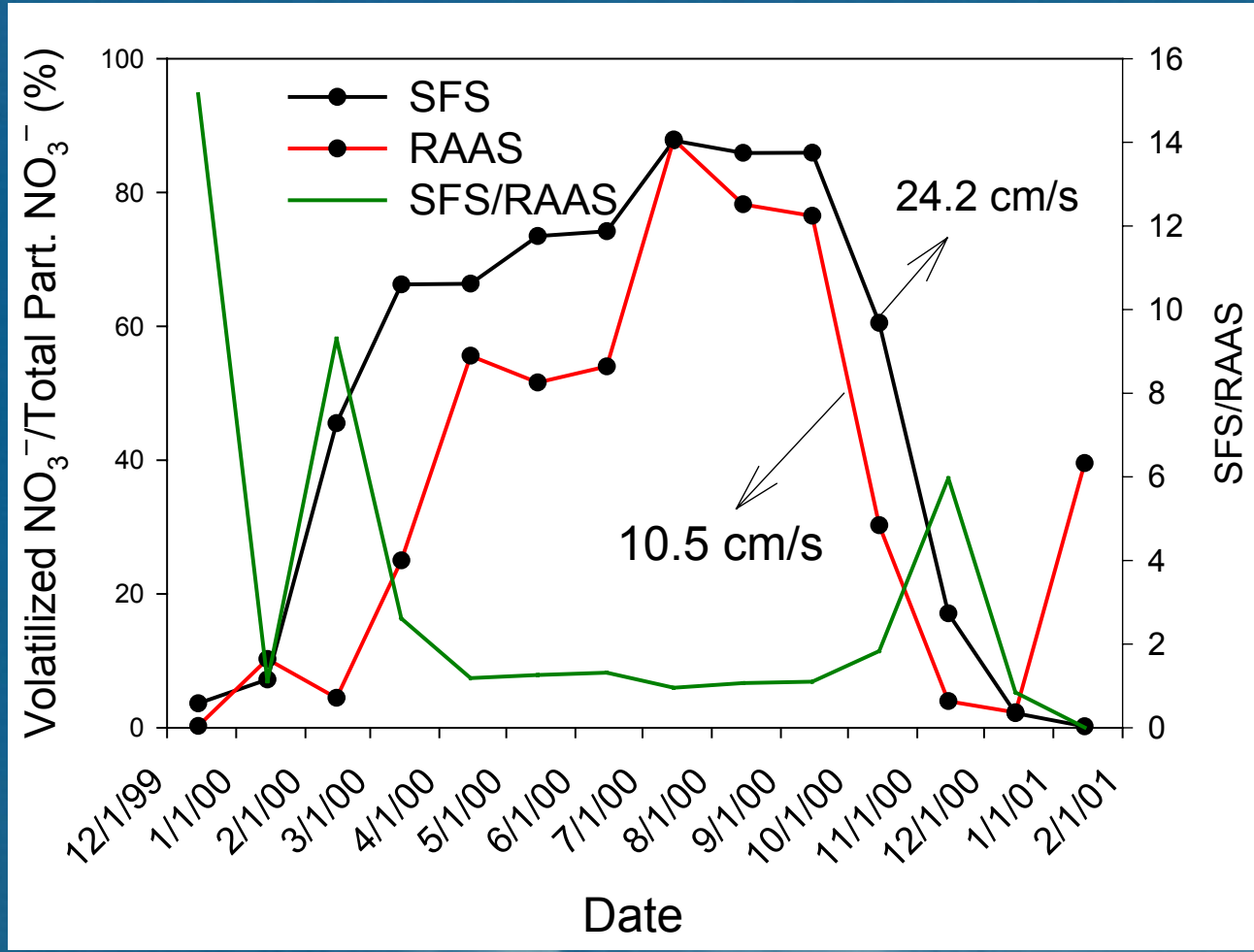
FALL INTENSIVE DAILY NITRATE VOLATILIZATION

Degree of volatilization decreases with temperature at both sites through the episode.



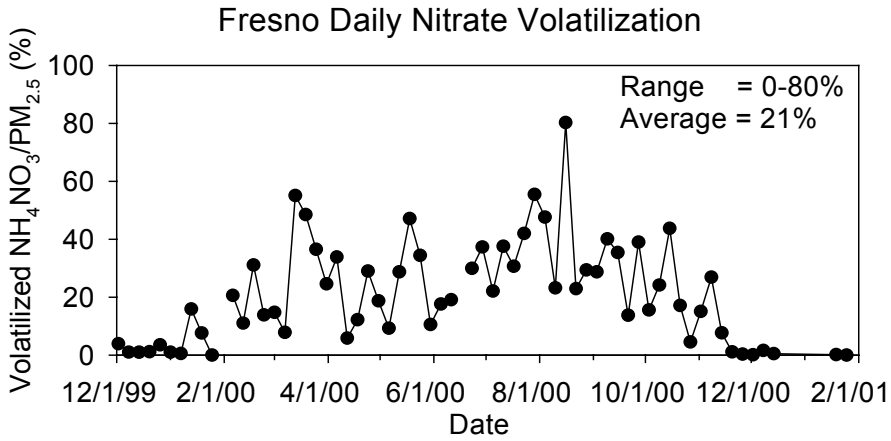
MONTHLY AVERAGE NITRATE VOLATILIZATION

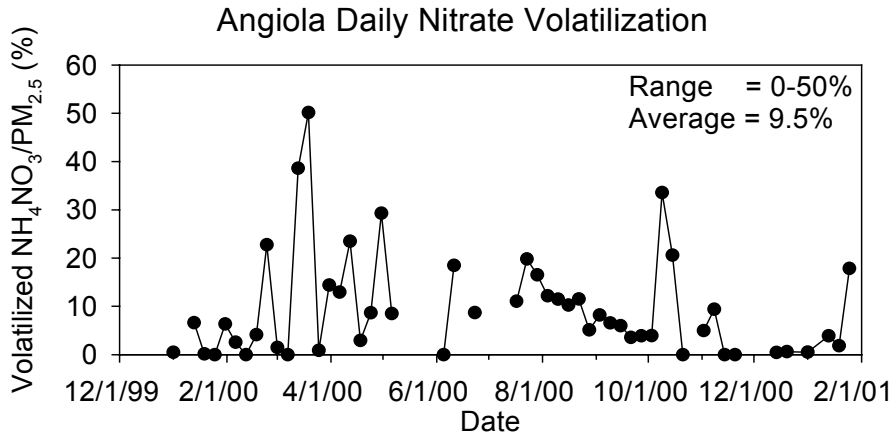
SFS (higher face velocity) volatilizes more nitrate than the RAAS sampler (lower face velocity).

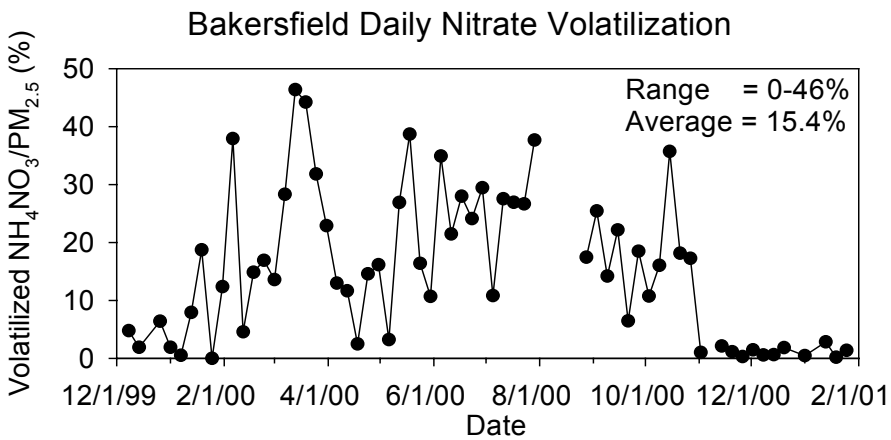


VOLATILIZED NH_4NO_3 NOT MEASURED BY GRAVIMETRIC MASS

$PM_{2.5}$ mass is underestimated by up to 80% on a daily basis due to nitrate volatilization.

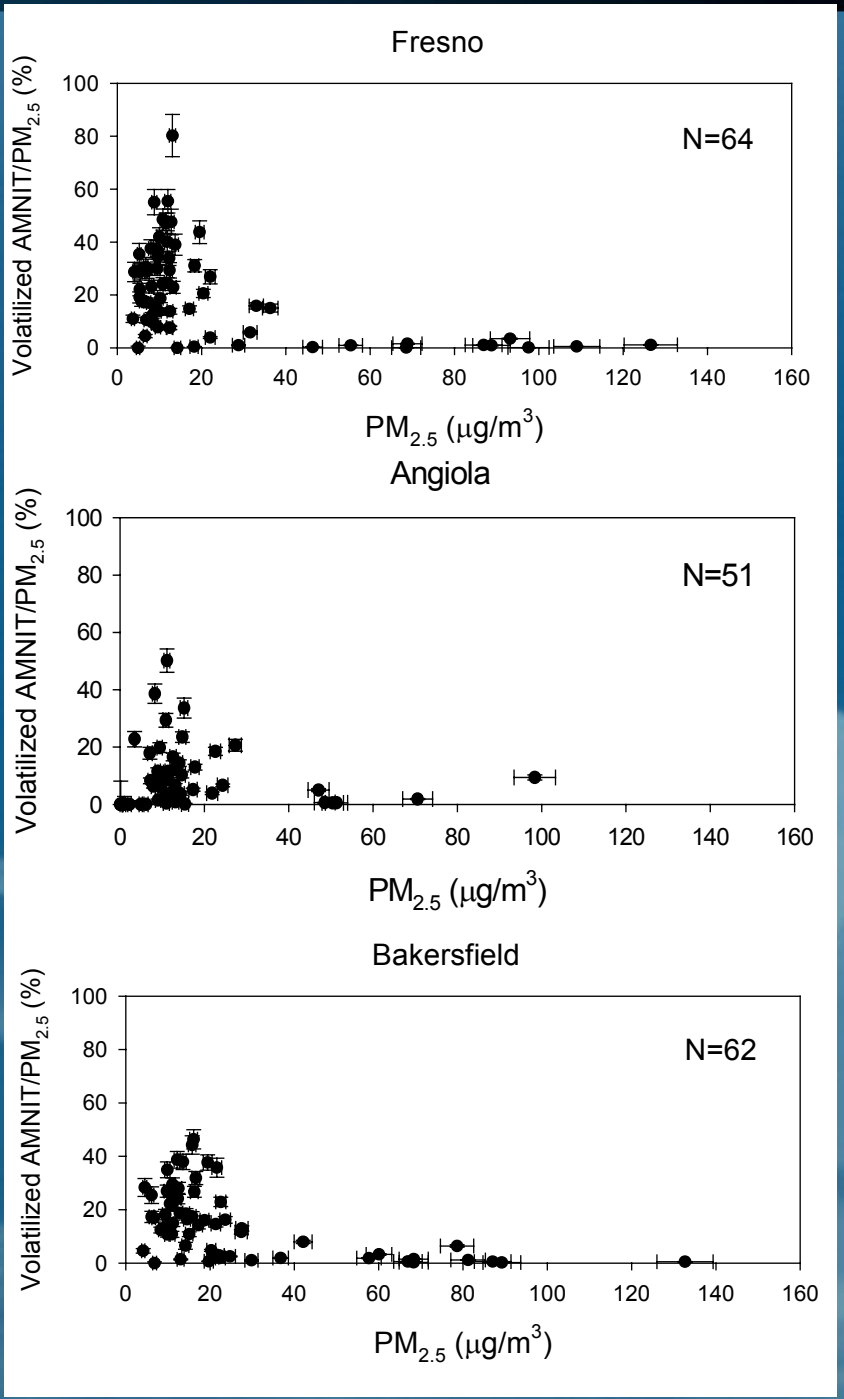






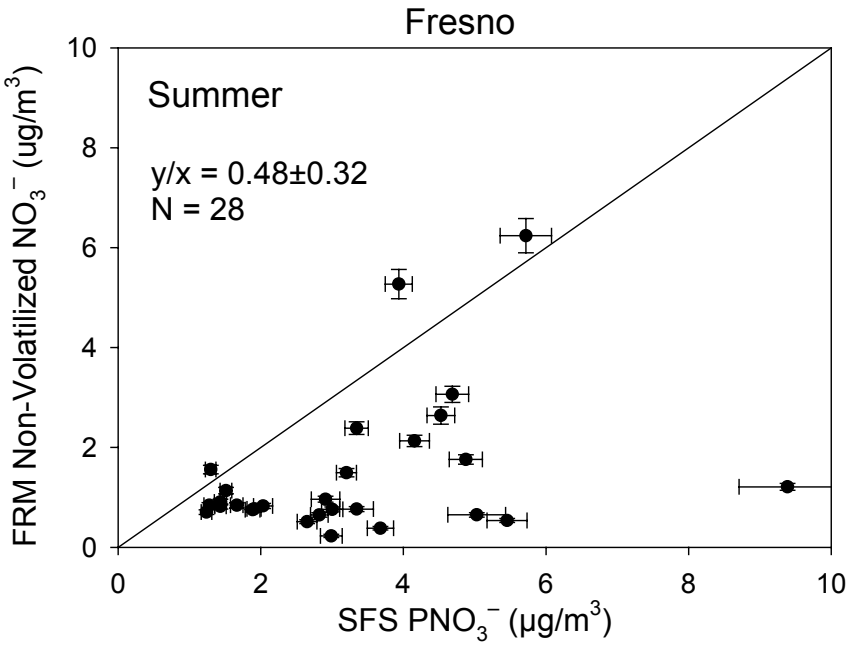
VOLATILIZED NH_4NO_3 NOT MEASURED BY GRAVIMETRIC MASS

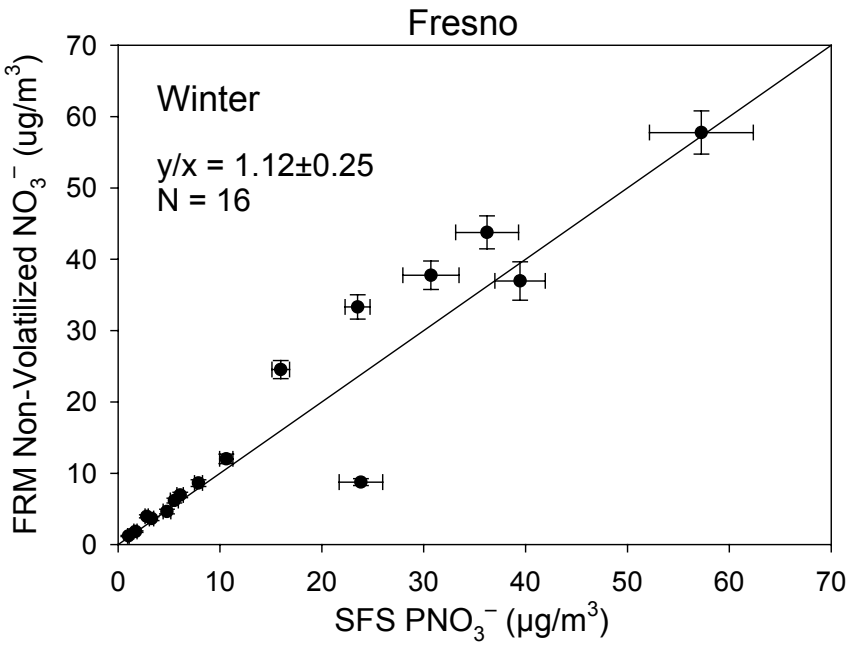
Nitrate volatilization exceeded 20% only when $PM_{2.5}$ < 20-30 µg/m^3.



In summer,
SFS PNO_3^- > FRM NO_3^-
4.8 > 2.4 μg/m^3
(average)

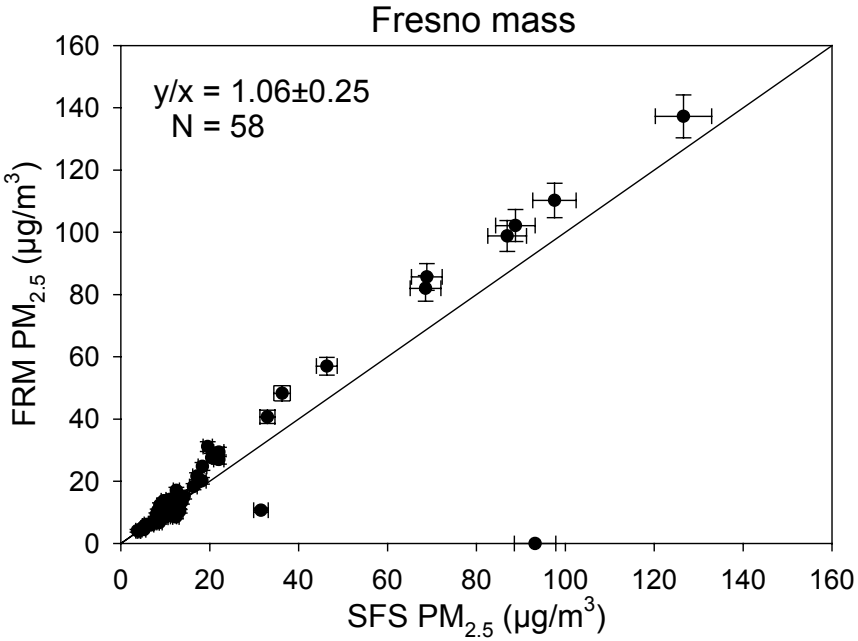
In winter,
SFS PNO_3^- < FRM NO_3^-
13 < 16 μg/m^3
(average)

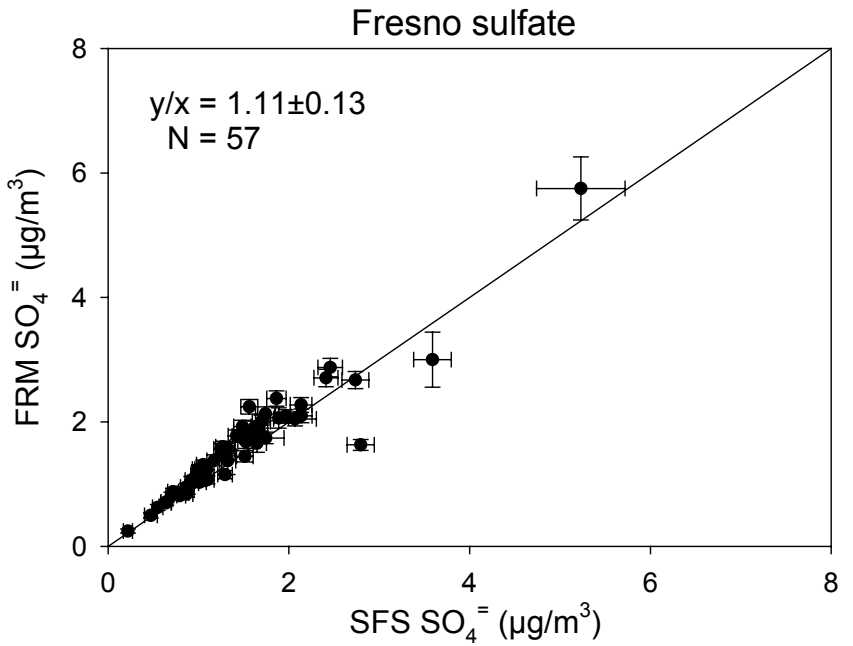




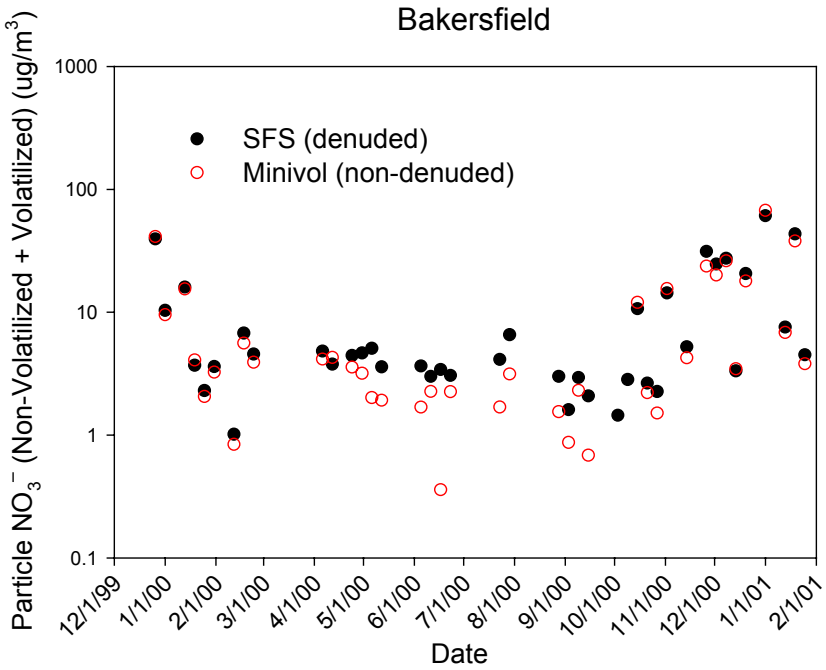
$PM_{2.5}$ mass and sulfate for FRM are systematically higher than SFS.

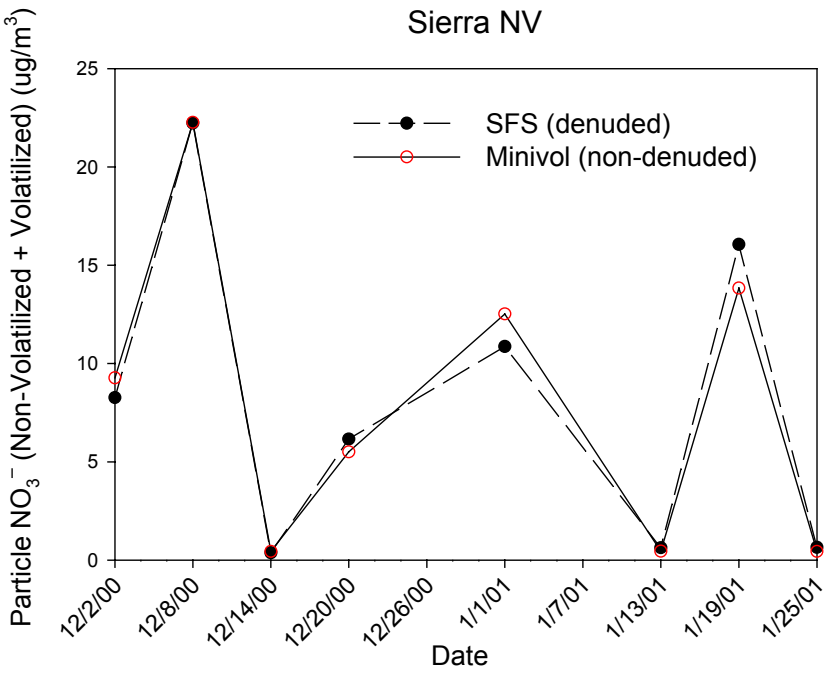
This could explain in part why winter FRM non-volatilized NO_3^- is higher than SFS total particulate NO_3^-.





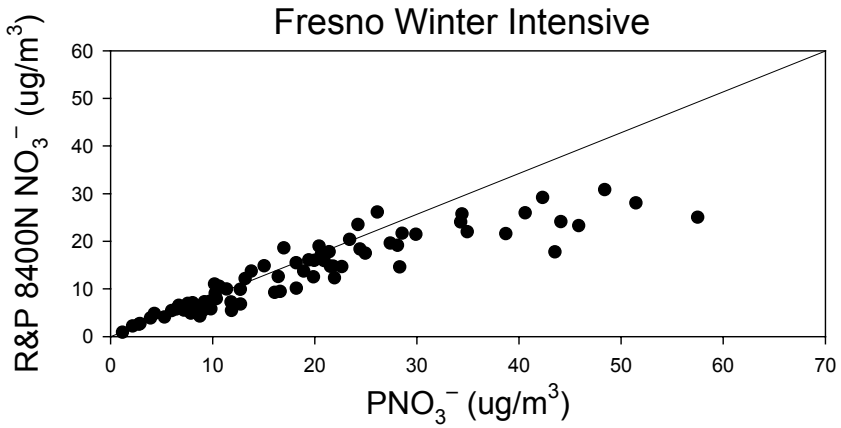
SFS particulate (denuded) nitrate is higher than Minivol (undenuded) nitrate in summer, but similar in winter.

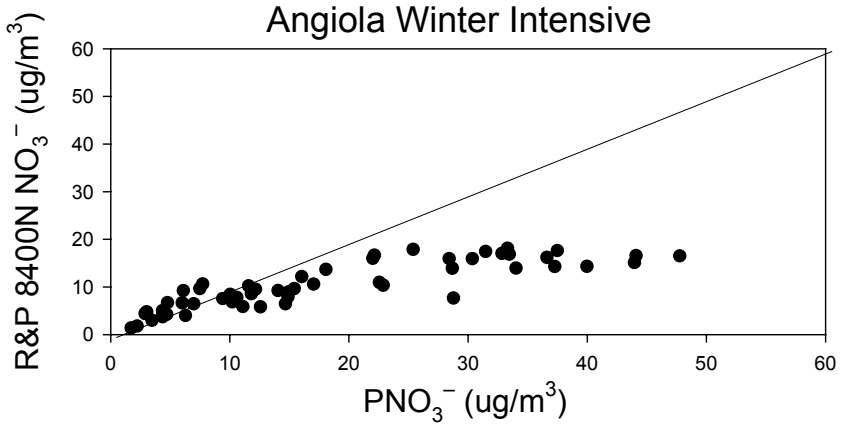


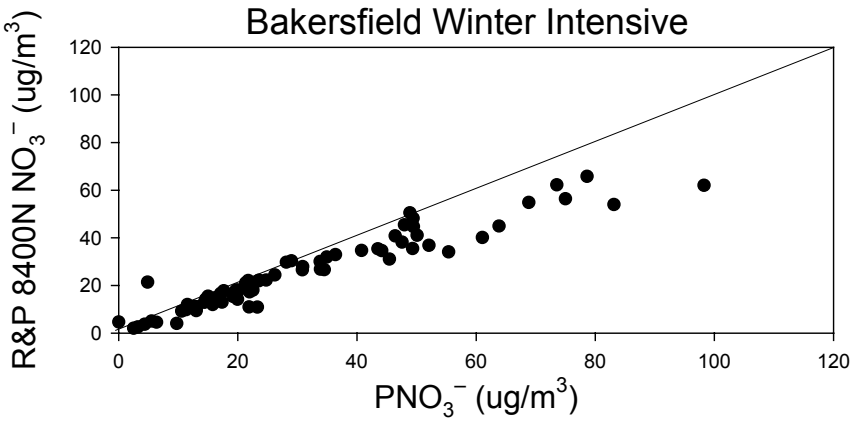


SFS PNO_3^- and R&P NO_3^- agree up to 20-30 ug/m^3, but R&P NO_3^- is lower at higher concentrations – most strongly at Angiola, least at Bakersfield.

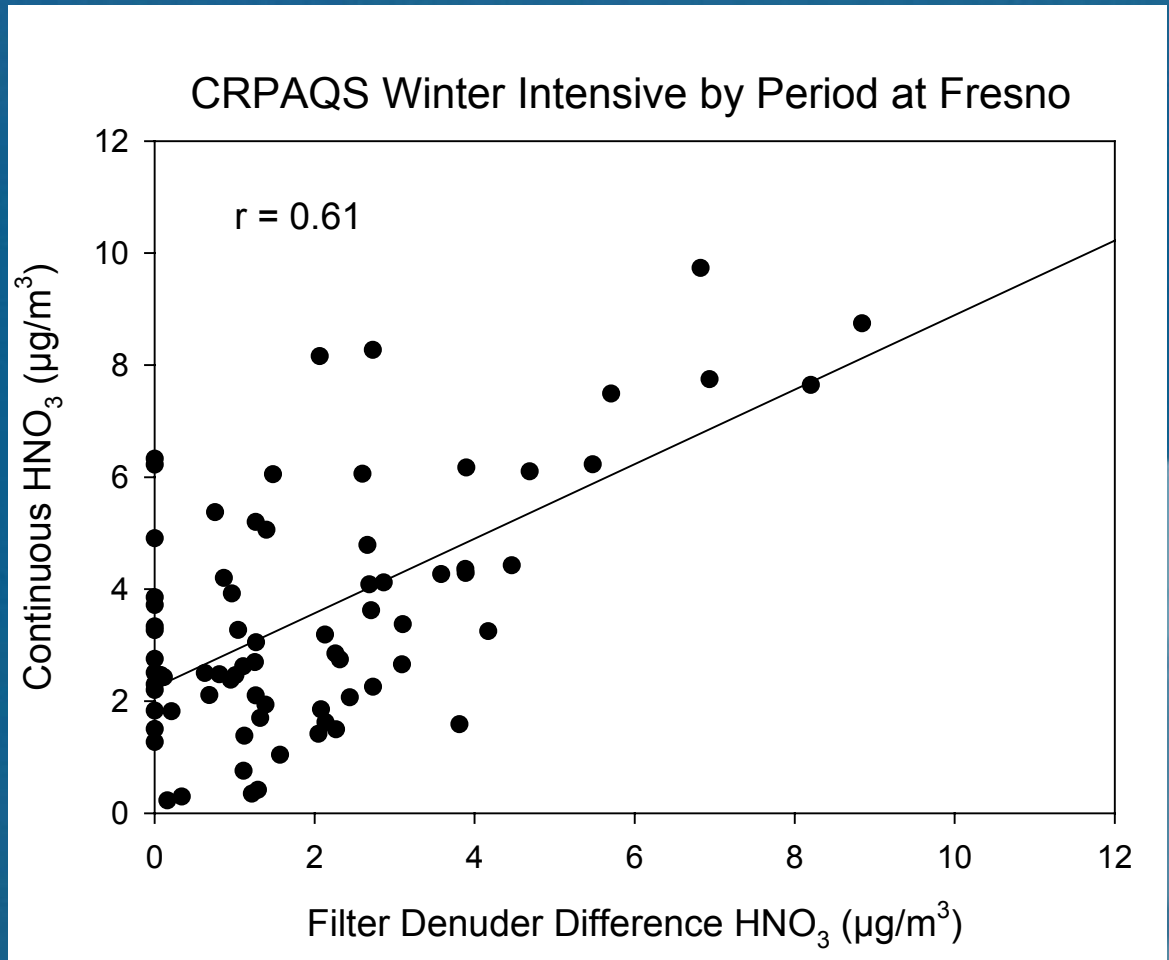
This may be related to the difference between ambient and R&P sampling temperature.



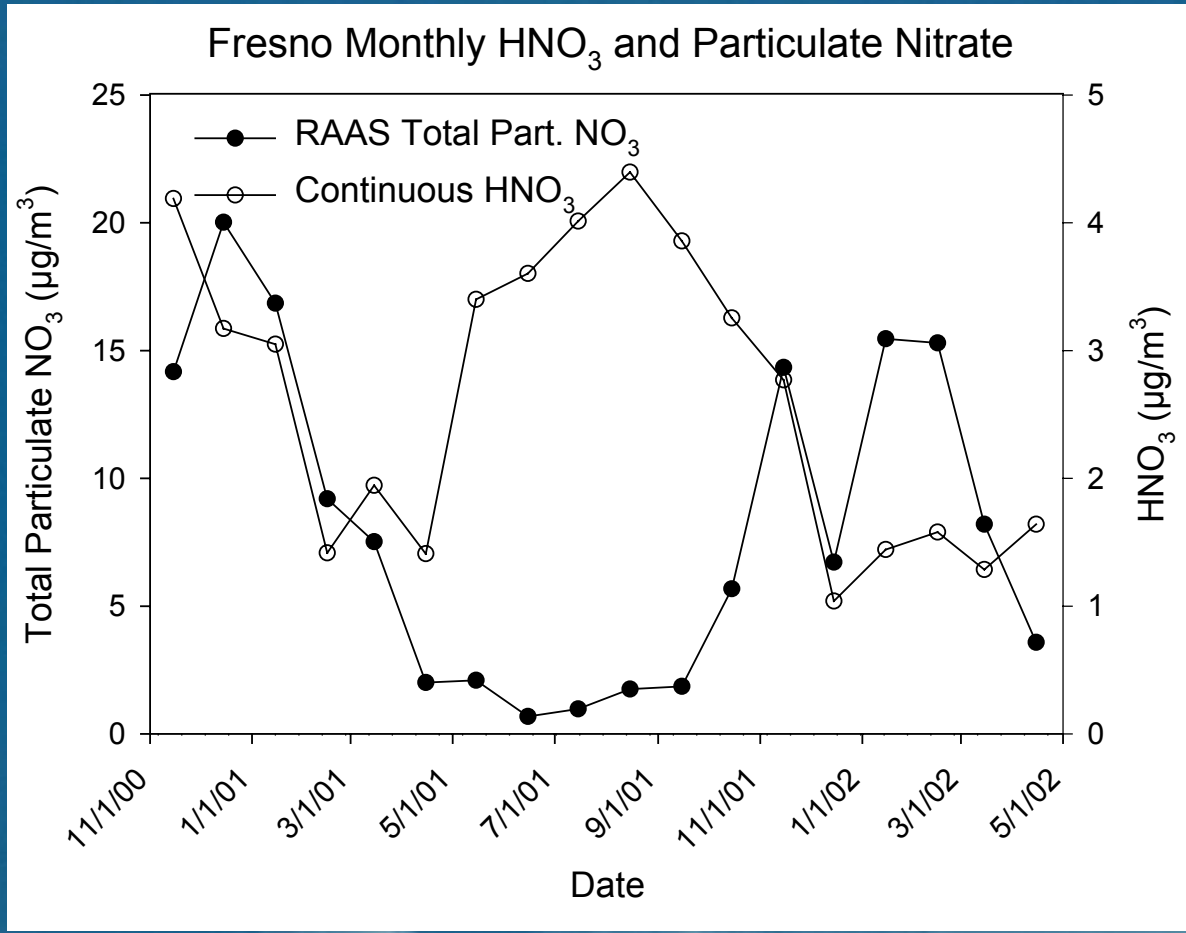




Continuous and filter HNO_3 by denuder difference are only moderately correlated.



PNO_3^- peaks in winter, while HNO_3 peaks in summer when it is dominant, as expected thermodynamically.



CONCLUSIONS

- The degree of ammonium nitrate volatilization varies seasonally and diurnally with temperature.
- Ammonium nitrate volatilization also increases with sampling face velocity where the SFS (24.2 cm/s) > RAAS (10.5 cm/s).
- Volatilized ammonium nitrate is up to 80%, 50%, and 46% of measured daily $PM_{2.5}$ mass at Fresno, Angiola, and Bakersfield, respectively.
- Nitrate volatilization exceeds 20% only when $PM_{2.5}$ < 20–30 µg/m3.

CONCLUSIONS *(continued)*

- Total particulate nitrate measured by denuded SFS agreed well with un-denuded Minivol sampler non-volatilized and volatilized nitrate in winter but not in summer at Bakersfield.
- Continuous R&P nitrate agreed with SFS particle nitrate up to 20-30 μg/m^3 but was lower at higher concentrations.
- Filter-based nitric acid measured by denuder difference was moderately correlated (r=0.61) with continuous nitric acid in Fresno.
- Fresno gaseous nitric acid concentrations peaked at about 4 μg/m^3 in summer coinciding with the annual minimum in particle nitrate.